

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

REC'D 08 MAR 2006

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Applicant's or agent's file reference P1897PC00	FOR FURTHER ACTION See Form PCT/IPEA/416	
International application No. PCT/FI2004/000713	International filing date (day/month/year) 24.11.2004	Priority date (day/month/year) 27.11.2003
International Patent Classification (IPC) or national classification and IPC See Supplemental Box		
Applicant Fortum OYJ et al		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
- a. ☒ (sent to the applicant and to the International Bureau) a total of 3 sheets, as follows:
- ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
- ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
- b. ☐ (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) _____, containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

- | | | |
|-------------------------------------|--------------|---|
| <input checked="" type="checkbox"/> | Box No. I | Basis of the report |
| <input type="checkbox"/> | Box No. II | Priority |
| <input type="checkbox"/> | Box No. III | Non-establishment of opinion with regard to novelty, inventive step and industrial applicability |
| <input type="checkbox"/> | Box No. IV | Lack of unity of invention |
| <input checked="" type="checkbox"/> | Box No. V | Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement |
| <input type="checkbox"/> | Box No. VI | Certain documents cited |
| <input checked="" type="checkbox"/> | Box No. VII | Certain defects in the international application |
| <input type="checkbox"/> | Box No. VIII | Certain observations on the international application |

Date of submission of the demand 20.06.2005	Date of completion of this report 10-02-2006
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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/FI2004/000713

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Continuation of: Cover sheet

INTERNATIONAL PATENT CLASSIFICATION (IPC) :

B01J 23/40 (2006.01)

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/FI2004/000713

Box No. I Basis of the report

1. With regard to the language, this report is based on:

- ☒ the international application in the language in which it was filed
- ☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of:
- ☐ international search (Rules 12.3(a) and 23.1(b))
- ☐ publication of the international application (Rule 12.4(a))
- ☐ international preliminary examination (Rules 55.2(a) and/or 55.3(a))

2. With regard to the elements of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

- ☐ the international application as originally filed/furnished
- ☒ the description:
- pages 1 - 21 as originally filed/furnished
- pages* _____ received by this Authority on _____
- pages* _____ received by this Authority on _____
- ☒ the claims:
- pages _____ as originally filed/furnished
- pages* _____ as amended (together with any statement) under Article 19
- pages* 1 - 3 received by this Authority on 16-01-2006
- pages* _____ received by this Authority on _____
- ☒ the drawings:
- pages 1 - 2 as originally filed/furnished
- pages* _____ received by this Authority on _____
- pages* _____ received by this Authority on _____
- ☐ a sequence listing and/or any related table(s) – see Supplemental Box Relating to Sequence Listing.

3. ☒ The amendments have resulted in the cancellation of:

- ☐ the description, pages _____
- ☒ the claims, Nos. 1 - 7
- ☐ the drawings, sheets/figs _____
- ☐ the sequence listing (*specify*): _____
- ☐ any table(s) related to the sequence listing (*specify*): _____

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages _____
- ☐ the claims, Nos. _____
- ☐ the drawings, sheets/figs _____
- ☐ the sequence listing (*specify*): _____
- ☐ any table(s) related to the sequence listing (*specify*): _____

* If item 4 applies, some or all of those sheets may be marked "superseded."

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/FI2004/000713

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	<u>1-16</u>	YES
	Claims		NO
Inventive step (IS)	Claims	<u>1-16</u>	YES
	Claims		NO
Industrial applicability (IA)	Claims	<u>1-16</u>	YES
	Claims		NO

2. Citations and explanations (Rule 70.7)

Reference is made to the following documents:

D1: US2001048970

D2: WO9110510

D3: Lashdaf M. et.al., Deposition of palladium and ruthenium beta-diketonates on alumina and silica supports in gas and liquid phase, Applied Catalysis A 241, 51-63 (2003)

D4: Dossi C. et.al., Chemical vapor deposition of platinum hexafluoroacetylacetonate inside KL Zeolite: A new route to nonacidic platinum-in-zeolite catalysts, Journal of catalysis 145, 377-383 (1994)

D5: US6235962

D6: WO0040676

D7: WO0208156

The invention relates to a method for producing a noble metal catalyst comprising the steps of pre-treating a zeolite with medium or large pore size, deposition of a noble metal by gas phase deposition and a heat treatment. The noble metals used in the production are platinum, palladium, ruthenium, rhodium, iridium and mixtures thereof. The invention relates to the use of said catalyst and ~~production~~ of a middle distillate diesel fuel.

Document D1 relates to a method for producing Pd/Au shell catalysts by chemical vacuum deposition, CVD (see section 19). As supports, it is possible to use inert materials such as SiO₂, Al₂O₃, TiO₂, ZrO₂, MgO or mixtures of SiC and Si₃N₄ (see claim 4).

Document D2 relates to the use of saturating gas-solid

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Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Continuation of: BOX V

reactions in a gas phase process, for the manufacture of a heterogeneous catalyst. The main groups of catalysts are represented by zeolite supported zinc, alumina-supported rhenium and silica supported chromium. The process comprises an optional pre-treatment step wherein the support is heated (see claim 6). Then the surface activated support is contacted and allowed to interact with vapour containing the catalytically active species or its precursor, then optional after-treatment follows (see claim 1).

Document D3 relates gas solid reactions for the deposition of vaporised Pd and Ru beta-diketonates on alumina and silica supports (see section 2.1). The metals are deposited on a preheated support with nitrogen as carrier gas. After deposition the samples are reduced.

Document D4 relates to the decomposition of volatile organometallic precursors inside zeolites. Pt/KL catalysts are prepared from platinum hexafluoro acetylacetonate precursors (see Catalyst preparation). The support is pre-heated and the deposition is performed in a flow of argon. Subsequent decomposition is also performed.

Document D5 relates to heterogeneous catalysts for ring-opening reactions of cyclic organic compounds such as naphthalene present in diesel fuel. The catalyst comprises catalytically active metal such as platinum on a carrier of alumina, silica or zirconia (see column 2, line 1-38). The hydrocarbons are introduced in a reactor under a pressure of 1 to 100 atm and a temperature from 450 to 670 K (see column 2, line 24-34).

Document D6 relates to the production of diesel fuel by ring-opening of naphthalene. Platinum on large pore crystalline zeolite (e.g. mordenite) supports is used (see page 5, line 1-16 and page 6, line 10-16). Pressure ranges will vary from 400 to 1000 psi, and reaction temperatures will range from 288 to 370 C depending on the feedstock (see page 5, line 17-26).

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Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of: BOX V

Document D7 relates naphthalene ring-opening catalysts comprising metals, such as platinum supported on inorganic oxides such as alumina or silica (see section 0025 and 0026). Preferred process conditions include temperatures from 150 C to 400 C and pressures from 100 to 3000 psi (see section 0029).

D2 is considered to be the closest prior art.

The method for manufacturing a catalyst according to claim 8 differs from D2 in that the noble metals platinum, palladium, ruthenium, rhodium, iridium and mixtures thereof is used in the production. The problem to be solved by the present invention may therefore be regarded as producing a catalyst with high selectivity for ring-opening reactions. No teaching of specific catalysts that promote ring-opening reactions is suggested in D2 and none of the above mentioned noble metals are suggested.

Therefore, claim 1 is considered to involve an inventive step. The use of said catalyst according to claim 15 and the production of a middle distillate diesel fuel in the presence of said catalyst according to claim 16 are also considered to involve an inventive step in view of the cited documents.

Accordingly, the invention defined in claims 1-16 is novel and is considered to involve an inventive step. The invention is industrially applicable.

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/FI2004/000713

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

Reference is in the description made to documents WO0008156, WO0008157 and WO0008158. However, it is assumed that the references instead should be WO0208156, WO0208157 and WO0208158.

Claims /PCT/FI2004/000713/ 16.01.2006

1. A method for the manufacture of a noble metal catalyst for hydrocarbon conversion, **characterized** in that the method comprises the following steps:
 - a) Pre-treatment of a support comprising a zeolite selected from medium and large pore zeolites having acid sites, at a temperature between 423 – 1173 K, and optional modification of the support;
 - b) Deposition of a noble metal selected from platinum, palladium, ruthenium, rhodium, iridium and mixtures and combinations thereof by gas phase deposition technique comprising vaporisation of the noble metal precursor selected from β -diketonates and metallocenes and reaction with the support, and
 - c) Heat treatment at oxidising or reducing conditions.
2. The method according to claim 1, **characterized** in that the noble metal is platinum.
3. The method according to claim 1 or 2, **characterized** in that the zeolite is selected from large pore zeolites having weak or medium strength of acid sites.
4. The method according to any one of claims 1 - 3, characterized in that the zeolite is selected from mesoporous aluminosilicates, crystalline aluminosilicates, crystalline aluminophosphates and crystalline aluminosilicophosphates.
5. The method according to any one of claims 1 - 4, characterized in that the zeolite is selected from MCM-41, Y- and beta-zeolites, mordenites, AlPO-5 and AlPO-11, SAPO-5 and SAPO-11.
6. The method according to any one of claims 1 - 5, **characterized** in that the support further comprises inorganic oxide, carbon related material or mixtures or combinations thereof.
7. The method according to claim 6, **characterized** in that the inorganic oxide is selected from silicon oxide, aluminum oxide, titanium oxide, zirconium oxide, tungsten oxide and magnesium oxide, preferably from silicon oxide and aluminum oxide.

8. The method according to claim 6, **characterized** in that the carbon related material is selected from activated carbon, graphite and carbon nanotubes.
9. The method according to any one of claims 1 - 8, **characterized** in that the noble metal precursor is $(\text{CH}_3)_3(\text{CH}_3\text{C}_5\text{H}_4)\text{Pt}$.
10. The method according to any one of claims 1 - 9, **characterized** in that the zeolite is MCM-41.
11. The method according to any one of claims 1 - 10, **characterized** in that in the first process step a) the support is pre-treated at a temperature of 423–1173 K, and in the second step b) the deposition is carried out in the presence of an inert carrier gas.
12. The method according to claim 11, **characterized** in that the inert carrier gas is nitrogen, helium, argon or methane.
13. The method according to any one of claims 1 - 12, **characterized** in that the modification in the first step a) is carried out by blocking part of available surface sites on the support with a blocking agent selected from alcohols, acetyl acetone, 2,2,6,6-tetramethyl-3,5-heptanedione, precursors of silicon oxide, aluminum oxide, titanium oxide, zirconium oxide, tungsten oxide and magnesium oxide, and nitrates.
14. The method according to claim 13, **characterized** in that the blocking agent is silicon tetrachloride, tetramethoxysilane, tetraethoxysilane, hexamethyldisilazane, hexamethyldisiloxane, aluminum chloride, aluminum ethoxide, aluminum (III) acetylacetonate, tris(2,2,6,6-tetramethyl-3,5-heptanedionato)aluminum, trimethyl aluminum, triethyl aluminum, titanium tetrachloride, titanium isopropoxide, zirconium tetrachloride, tungsten oxychloride, tungsten hexachloride or tris(2,2,6,6-tetramethyl-3,5-heptanedionato) magnesium.
15. Use of the noble metal catalyst manufactured according to the method of any one of claims 1 - 14 in ring-opening, isomerisation, alkylation, hydrocarbon reforming, dry reforming, hydrogenation and dehydrogenation reactions, and preferably in ring-opening of naphthenic molecules.

16. A process for the manufacture of middle distillate diesel fuel, **characterized** in that a middle distillate feedstock is transferred to a reactor wherein it is allowed to react at a temperature of 283 - 673 K and under a pressure of 10 – 200 bar with hydrogen in the presence of a noble metal catalyst manufactured according to the method of any one of claims 1-14 to accomplish opening of naphthenes with two and multiple rings to produce isoparaffins, n-paraffins and mononaphthenes in the middle distillate region.